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Thiosulfate as an Oxidation Inhibitor in Flue Gas Desulfurization Processes A Review of R and D Results

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16. ABSTRACT The article describes the pilot-plant testing of sodium thiosulfate ($Na_2S_2O_3$) as an oxidation inhibitor in flue gas desulfurization by lime and limestone slurry scrubbing with and without MgO and adipic acid additives. The effectiveness of thiosulfate is proportional to the inhibitor product, defined as the product of thiosulfate concentration (M), calcium concentration (M), and the moles of SO_2 absorbed per hour per liter of hold tank volume. Gypsum saturation was less than 100% and scaling was eliminated when the inhibitor product exceeded 0.3 times 10 to the minus 6 times M to the 3rd power. Thiosulfate was relatively more effective in systems with chlorides and less effective in systems promoted by MgO. An inhibitor product greater than 10 to the minus 6 times M to the 3rd power/hr significantly enhanced dewatering of solids from limestone scrubbing. SO_2 removal and/or limestone utilization were increased in systems that started with less than 10 mM dissolved calcium.

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Thiosulfate as an Oxidation Inhibitor in Flue Gas Desulfurization Processes: A Review of R&D Results

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Sodium thiosulfate ($Na_2S_2O_3$) has been tested in a pilot plant as an oxidation inhibitor in flue gas desulfurization by lime and limestone slurry scrubbing with and without MgO and adipic acid additives. The effectiveness of thiosulfate is proportional to the inhibitor product, defined as the product of thiosulfate concentration (M), calcium concentration (M), and the moles of SO_2 absorbed per hour per liter of hold tank volume. Gypsum saturation was less than 100 percent and scaling was eliminated when the inhibitor product exceeded 0.3 $\times 10^{-6}$ (gmol/L)^3/h. Thiosulfate was relatively more effective in systems with chlorides and less effective in systems promoted by MgO. An inhibitor product greater than 10^{-6} (gmol/L)^3/h significantly enhanced dewatering of solids from limestone scrubbing. SO_2 removal and/or limestone utilization were increased in systems that started with less than 10 mM dissolved calcium.

Sulfite oxidation is an important side reaction in flue gas desulfurization processes using aqueous solutions. In slurry scrubbers using lime or limestone, gypsum ($CaSO_4 \cdot 2H_2O$) scaling on scrubber internals and mist eliminators has in many cases been a serious reliability problem. Thiosulfate ($S_2O_3^=$) has been identified and tested as an effective oxidation inhibitor in slurry scrubbing systems. It reduces gypsum saturation and thereby reduces scaling. It also enhances the dewatering properties of calcium sulfite solids, enhances SO_2 removal when used with MgO, and reduces oxidative degradation of organic acid additives.

This paper is a review of research and development results on thiosulfate as an oxidation inhibitor in flue gas desulfurization. New pilot plant results are also presented on the effectiveness of thiosulfate in five lime/limestone slurry scrubbing processes.

Table I is a chronological summary of the work on thiosulfate. Thiosulfate was recognized as an oxidation inhibitor in early work by the Tennessee Valley Authority (TVA)[1] and Fuji Electric Company.[3] In 1978, Radian Corporation rediscovered it as the oxidation inhibitor present with carbide lime and responsible for the scale-free operation of a scrubber operated by Louisville Gas and Electric.[4] Further development was slowed by negative results with lime scrubbing in the Environmental Protection Agency (EPA) pilot plant at Research Triangle Park (RTP).[5] Nevertheless, in 1979 Duquesne Light successfully started adding sodium thiosulfate to eliminate gypsum scaling and enhance SO_2 removal in a 387 MW scrubber system using magnesium-promoted lime.[7]

In 1981, laboratory work at the University of Texas[8] demonstrated that as little as 1 millimolar (mM) thiosulfate would practically stop sulfite oxidation and adipic acid degradation at pH 5. One test at 10 mM thiosulfate with limestone slurry in the 10-MW spray scrubber at TVA's Shawnee Station drastically reduced sulfite oxidation and enhanced solids dewatering, but the thiosulfate appeared to degrade rapidly.[10] In 1982 extensive testing at Shawnee[11] showed that thiosulfate was effective at 1 mM in reducing gypsum saturation and at 3 mM in enhancing dewatering of the waste solids. Battelle[14] identified trithionate as the primary thiosulfate degradation product. In 1983–84, laboratory work at the University of Texas quantified sulfite oxidation and thiosulfate degradation as a function of solution composition.[17]

In 1983–84, extensive testing was performed in the EPA-RTP pilot plant in a turbulent contact absorber (7.5 m^3/min gas rate) with lime and limestone slurry with and without magnesium and organic acid additives. These results quantified the effect of thiosulfate on gypsum saturation and solids dewatering and demonstrated that thiosulfate addition is generally useful in any slurry scrubbing process not using forced oxidation. In this paper further analysis of these and previous results is given to quantify the effects of thiosulfate and the makeup requirements.

In 1985, use of thiosulfate was initiated by Seminole Electric Cooperative in its 1240-MW plant at Palatka, Florida.[20] This system uses thiosulfate to eliminate gypsum scaling and enhance solids dewatering in a limestone slurry scrubber.

Effects of Thiosulfate

Thiosulfate has been tested extensively in limestone slurry scrubbing at Shawnee and RTP. At RTP, additional testing has also been performed in limestone scrubbing promoted by MgO and by adipic acid and in lime scrubbing alone

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and promoted by MgO. These systems all had SO_2 inlet gas concentrations of 2000–3000 ppm.

Without thiosulfate, all of the processes operated with sulfite oxidation of 17–20 percent and gypsum saturation greater than 100 percent. Significant gypsum scaling was observed with lime and limestone alone and light scaling with addition of $MgSO_4$ or adipic acid. With the lowest maintainable thiosulfate concentration, 0.9 mM, all of the processes operated with less than 100 percent gypsum saturation and no gypsum scaling. At higher thiosulfate levels solids dewatering was enhanced using limestone with or without adipic acid, and SO_2 removal or limestone utilization was improved slightly in all of the processes except lime scrubbing. Thiosulfate was generally more effective in the limestone systems when chloride was present at higher levels.

Sulfite Oxidation

The primary effect of thiosulfate is to inhibit sulfite oxidation. Laboratory measurements have quantified the effects of solution composition on the rate of sulfite oxidation. Pilot plant data from EPA-RTP and Shawnee include measurement of solids oxidation; however, the analytical precision is poor at low oxidation levels and cannot be used to quantify this primary effect.

Thiosulfate appears to function as a free radical scavenger rather than a complexer of S(IV) (sulfite plus bisulfite) or metal ions. Its effective concentration is much less than S(IV); therefore, it probably does not form an unoxidizable complex with S(IV). Using literature values for the chelating constant $\{[\text{Fe chelate}]/([Fe^{+++}][S_2O_3^{=}]) = 447\ M^{-1}\}$,[21] only 50 percent of the Fe^{+++} should be chelated with 1 mM thiosulfate. Other metals are even less strongly chelated. Furthermore, thiosulfate appears to degrade as it functions, consistent with a role as a free radical scavenger, but inconsistent with complexing.

A probable mechanism for S(IV) oxidation in the presence of thiosulfate includes some constant rate of free radical initiation catalyzed by Fe(r_i), a limiting propagation reaction such as,

$$SO_3^{=} + SO_4^{-} \rightarrow SO_3^{-} + SO_4^{=} \quad (1)$$

$$r_{ox} = k_{ox}[SO_3^{=}][SO_4^{-}] \quad (2)$$

and a termination reaction limited by thiosulfate and giving tetrathionate,

$$S_2O_3^{=} + SO_4^{-} \rightarrow S_2O_3^{-} + SO_4^{=} \quad (3)$$

$$2S_2O_3^{-} \rightarrow S_4O_6^{=} \quad (4)$$

$$r_t = k_t[S_2O_3^{=}][SO_4^{-}] \quad (5)$$

The thiosulfate radical has been studied by Hayon,[22] and oxidation of thiosulfate by iodine or other oxidants typically gives tetrathionate.[23] Assuming that $r_i = r_t$, this oxidation mechanism gives a rate equation of the form:

$$r_{ox} = (r_i k_{ox}/k_t)([SO_3^{=}]/[S_2O_3^{=}]) \quad (6)$$

By substituting the equilibrium of sulfite and bisulfite and assuming that S(IV) is mostly bisulfite, valid for pH less than 6:

$$[SO_3^{=}] = K_a[HSO_3^{-}]/[H^+] = K_a[S(IV)]/[H^+] \quad (7)$$

$$r_{ox} = (r_i k_{ox} K_a/k_t)([S_2O_3^{=}][H^+]/[S(IV)])^{-1} \quad (8)$$

Because most of the solutions are approximately saturated with calcium sulfite, Equation 6 can also be expressed in terms of Ca^{++} concentration by substituting the solubility relationship:

$$[SO_3^{=}] = K_{sp}/[Ca^{++}] \quad (9)$$

Using *Ldg* to represent the moles of SO_2 absorbed per hour per liter of hold tank volume(M/h), the fraction oxidation, f_{ox}, is equal to r_{ox}/Ldg and is given by combining Equations 6 and 9:

$$f_{ox} = (r_i K_{sp} k_{ox}/k_t)/([Ca^{++}][S_2O_3^{=}]Ldg) \quad (10)$$

where the product of calcium, thiosulfate, and loading is defined as the inhibitor product.

Owens[17] measured the rate of sulfite oxidation by air in a vigorously stirred solution of 0.3 M Na_2SO_4 at 50°C with pH 4.5 to 6, 3 to 30 mM S(IV) (total sulfite plus bisulfite), 0.1 to 9.5 mM sodium thiosulfate, and 0.001 to 0.05 mM Fe^{++}. When the ratio of thiosulfate to S(IV) is greater than 0.1, Figure 1 shows that his results are correlated by Equation 8 with the coefficient given by:

$$r_i k_{ox} K_a/k_t = 10^{-9} M^2/h \quad (11)$$

The rate of oxidation is approximately independent of oxy-

Table I. Chronological summary of work with thiosulfate.

Date	Organization	Scale	Results
1972	TVA[1]	lab	7 mM (millimolar) thiosulfate stopped sulfite oxidation at pH 5
1972	Louisville Gas and Electric[2]	150 MW	Carbide lime at Paddy's Run gives low oxidation and scale-free operation
1974	Fuji Electric[3]	lab	Thiosulfate inhibits sodium sulfite oxidation (patent)
1977	Radian[4]	lab	Identifies thiosulfate as probable inhibitor at Paddy's Run
1978	EPA[5]	pilot	Thiosulfate appears ineffective with lime
1979	U. of Va.[6]	lab	0.2 mM thiosulfate practically stops oxidation at pH 4
1979	Duquesne Light[7]	pilot & 387 MW	0.002 mole thiosulfate/mole CaO stops scaling in MgO-promoted lime scrubber at Phillips station
1980	Duquesne Light[7]	494 MW	Thiosulfate used at Elrama station with MgO-promoted lime
1981	U. of Tx.[7,8,9]	lab	1 mM thiosulfate stops sulfite and organic acid oxidation
1981	Bechtel/TVA[10]	10 MW	10 mM thiosulfate inhibits oxidation and enhances dewatering in limestone scrubber but degrades
1981	Battelle[7]	lab	Confirm inhibition, review work to date
1982	TVA[11,12,13]	10 MW	In a limestone scrubber 1 mM thiosulfate inhibits oxidation, >3 mM enhances solids dewatering
1982	Battelle[14]	lab	Primary degradation product is trithionate
1983	U. of Tx.[15,16]	lab	Thiosulfate inhibits oxidation catalyzed by Mn better than by Fe
1984	U. of Tx.[17,18]	lab	Inhibition quantified; thiosulfate degrades initially at 1 mM/h
1984	Acurex/EPA[19]	pilot	Thiosulfate demonstrated to be effective with lime or limestone w/ or w/o DBA or MgO
1985	Peabody/Seminole Electric[20]	1240 MW	Thiosulfate eliminates scaling and enhances dewatering in limestone w/ and w/o DBA

gen and Fe^{++} concentration, although the rate was much slower with no Fe^{++} added. Manganese (Mn^{++}) did not appear to be a catalyst in the presence of thiosulfate.

In a slurry scrubbing system, the rate of oxidation should be a more complicated function of thiosulfate concentration. Without thiosulfate, oxidation is controlled by absorption of oxygen in the absorber, giving oxidation levels of 15–30 percent with flue gas from high sulfur coal. At moderate levels of thiosulfate, scrubber oxidation should be completely inhibited, but oxidation in the hold tank and thickener will be limited by the supply of oxygen. The minimum supply of oxygen to the hold tank is the solubility of oxygen in the solution at the scrubber outlet, typically about 0.1 mM at 10 percent oxygen in the flue gas. This corresponds to an oxidation level of about 2 percent. More oxygen will be available if the liquid surface in the hold tank is agitated and exposed to air. At high levels of thiosulfate, oxidation should be controlled by the reaction kinetics represented by Owens' results in Figure 1.

Oxidation rates for the RTP pilot plant have been calculated assuming that all of the oxidation occurs in the hold tank. Without thiosulfate the oxidation rates are typically 10–20 mM/h. With thiosulfate the oxidation rates vary from 0.5 to 4 mM/h and are correlated by Equation 8 as shown in Figure 1. The pilot plant data include variation in pH from 5 to 7.5 and in S(IV) from 1.6 to 44 mM. Figure 1 also shows previous results in the pilot plant on oxidation at dual alkali conditions [80 mM S(IV), pH 6.2].[24]

The correlation of Figure 1 represented by Equation 8 shows that more thiosulfate is required at higher levels of dissolved S(IV) and higher pH. In practice the level of S(IV) is increased in systems with added MgO or Na_2CO_3, along with a reduction in dissolved Ca^{++}. Therefore, a higher thiosulfate concentration is required to inhibit oxidation in dual alkali processes or slurry scrubbing processes promoted by MgO. Similarly, less thiosulfate is required in slurry scrubbing with high concentrations of $CaCl_2$, because the Ca^{++} reduces the level of dissolved S(IV).

Figure 2 illustrates the correlation of the fraction oxidation in the RTP pilot plant with the inhibitor product. In the pilot plant sulfate is formed not only by S(IV) oxidation but also by hydrolysis of trithionate, the degradation product of thiosulfate. Assuming that trithionate hydrolysis contributes a constant 2 percent oxidation (corresponding to a hydrolysis rate of 0.6 mM/h and SO_2 loading of 30 mM/h), the data are correlated by a modified form of Equation 9:

$$f_{ox} = 30 \times 10^{-9} M^3/h([Ca^{++}][S_2O_3^{=}]Ldg)^{-1} + 0.02 \quad (12)$$

To the extent that calcium concentration can be increased, the effectiveness of thiosulfate as an oxidation inhibitor should be increased.

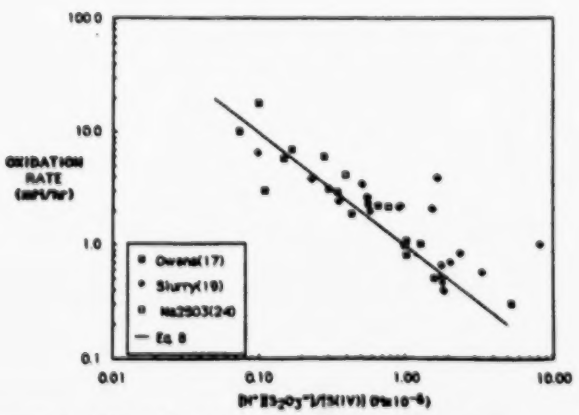

Figure 1. Sulfite oxidation rates at 50°C, inhibited by thiosulfate.

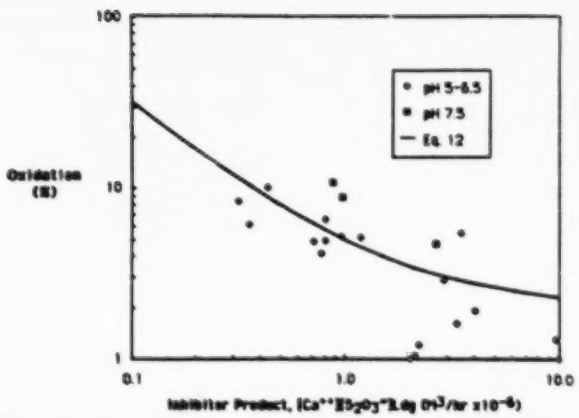

Figure 2. Effect of thiosulfate on solids fraction oxidation at the EPA-RTP pilot plant.[19]

Gypsum Saturation and Scaling

When slurry scrubbers operate with sulfite oxidation levels less than 15 or 20 percent of the SO_2 absorbed, gypsum scaling usually does not occur because the calcium sulfate precipitates as a solid solution with calcium sulfite hemihydrate, rather than as gypsum (calcium sulfate dihydrate). In this case the solution is unsaturated with gypsum. The relative gypsum ($CaSO_4 \cdot 2H_2O$) saturation (RS_{gyp}) was estimated from solution analyses, in moles/liter (M) by the correlation[25]:

$$RS_{gyp} = [Ca^{++}][SO_4^{=}](263/I + 47) \quad (13)$$

where I = ionic strength = $3[Ca^{++}] + 3[Mg^{++}] + [Na^+] + [SO_4^{=}] + [S_2O_3^{=}] + [S_3O_6^{=}]$

The equilibrium of aqueous solution with calcium sulfite solid solution is given in Figure 3 as aqueous solution composition (gypsum saturation) versus solid composition (mole percent oxidation). The solid curve, a correlation of laboratory data by Radian,[26] is given by the equation:

$$RS_{gyp} = f_{ox} \exp(-1.11 + 22.5 f_{ox}) \quad (14)$$

As shown in Figure 3, the RTP pilot plant data agree reasonably well with the Radian correlation. The greatest scatter in the data occurs at low oxidation levels where measurement of oxidation and gypsum saturation is very difficult. Sulfate content of the solids and solution is calculated by the difference between S(IV) determined by iodometric titration and the sum of sulfate and S(IV) determined by ion chromatography. Data from the Shawnee pilot plant using thiosulfate give an average solids oxidation of 15 percent with a gypsum saturation of only 13 percent, well below the Radian correlation, probably because of inaccurate solids analysis.

The effect of thiosulfate on gypsum saturation is shown more directly in Figure 4 which gives the effect of the inhibitor product, $[S_2O_3^{=}][Ca^{++}]Ldg$. Combining Equations 12 and 14 gives the relationship shown as the curve on Figure 4:

$$RS_{gyp} = |0.01 + 15.5 \times 10^{-9}/([Ca^{++}][S_2O_3^{=}]Ldg)| \times \exp|113 \times 10^{-9}/([Ca^{++}][S_2O^{=}]Ldg)| \quad (15)$$

Figure 4 includes data from RTP and Shawnee. The scatter of the data may result from difficulty in measuring gypsum saturation at low levels. The data from Shawnee generally fall above the RTP correlation. At Seminole Electric, the gypsum saturation varies from 5 to 20 percent with inhibitor product exceeding 20×10^{-6} M^3/h. One explanation for higher levels of saturation in the field units could be

additional "oxidation" contributed by absorption of SO_3 from the flue gas.

Solids Dewatering

The dewatering properties of calcium sulfite solids are improved by reducing their sulfate content. The crystallization of calcium sulfite is inhibited by increased gypsum saturation (dissolved calcium sulfate). Tseng[27,28] found that the growth rate of one crystal face is inhibited by sulfate and that the thickness of individual platelets increases as solid sulfate content decreases: 10 percent oxidation gave 0.01 μm platelets, 3 percent oxidation gave 0.1 μm platelets, and 1 percent oxidation gave 2 μm platelets. Chang *et al.*[24] found that dewatering properties of dual alkali solids were improved by operating at conditions giving lower levels of solids oxidation.

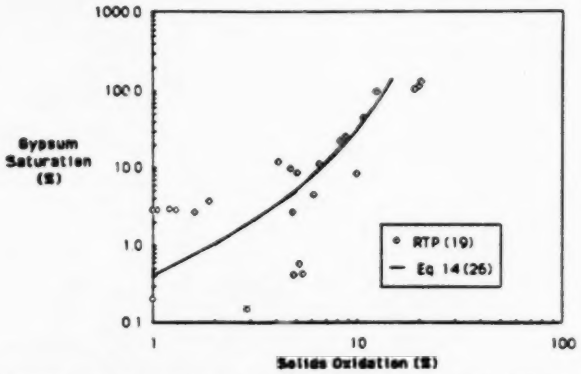

Figure 3. Equilibrium relationship of gypsum saturation with solids oxidation.

Improved dewatering has not been observed in any of the commercial plants using lime scrubbing. The initial work with limestone at Shawnee suggested that the filter cake solids content increased from 40 to 80 percent when operating with an excessive level of thiosulfate.[29] However, this observation was not included in the written report[10] because of uncertainties and unsteady state behavior associated with frequent changes in the dewatering configuration. Later work at Shawnee[11] using 2 mM thiosulfate showed a definite increase from 65 to 85 percent solids in the filter cake and from 0.35 to 0.65 cm/min initial settling rate when an inhibitor product greater than 10^{-6} M^3/h was used. These tests with 15 percent limestone scrubbing slurry included about 40 percent fly ash in the waste solids.

In the pilot plant work at RTP, thiosulfate addition enhanced filter cake solids from 56 percent to as high as 78 percent (Figure 5) and initial settling rate from 0.7 to as high

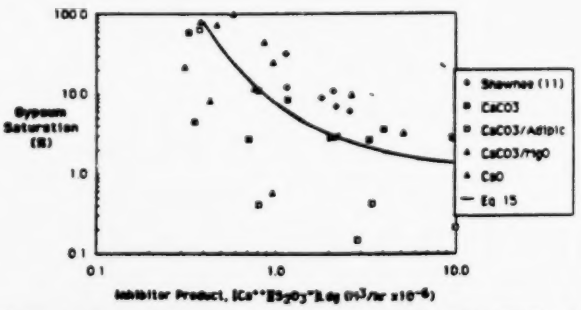

Figure 4. Effect of thiosulfate on gypsum saturation at the EPA-RTP[19] and Shawnee[11] pilot plants.

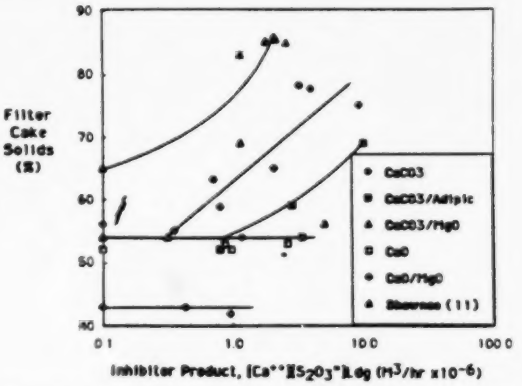

Figure 5. Effect of thiosulfate on filter cake solids at the EPA-RTP[19] (with various reagents) and Shawnee[11] (limestone) pilot plants.

as 3.6 cm/min (Figure 6). Dewatering enhancement was observed at RTP whenever the measured solids oxidation was less than 2 percent. Table II shows that mass mean particle diameter measured by a Coulter counter increased at higher inhibitor product with a resulting enhancement of dewatering properties. Run LS-5 was at a much higher inhibitor product because of the addition of calcium chloride. Pictures of solids from the three runs in Table II taken with a scanning electron microscope show that the solids appear to change from thin platelets to bulky crystals as solids oxidation is inhibited.

With limestone alone, dewatering was enhanced at an inhibitor product greater than 3×10^{-6} M^3/h, usually achieved with addition of both thiosulfate and calcium chloride. The RTP tests were made without fly ash, which may have enhanced the dewatering effect at Shawnee.

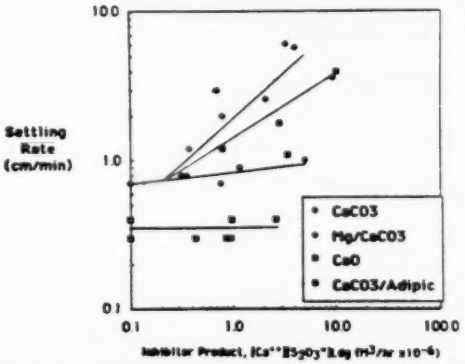

Figure 6. Effect of thiosulfate on the initial settling rate of product solids at the EPA-RTP pilot plant with various reagents.

Using limestone with 15 mM adipic acid, dewatering enhancement was not observed at an inhibitor product of 3.5×10^{-6} M^3/h but was observed at 10.5×10^{-6} M^3/h. It is known that adipic acid coprecipitates with calcium sulfite in the same way that sulfate does,[30,31] and it may also inhibit crystal growth.

No dewatering enhancement was observed with limestone scrubbing using Mg promotion or with lime scrubbing; however, the inhibitor product did not exceed 5×10^{-6} M^3/h in any of these series. In these lime/limestone systems high concentrations of thiosulfate are needed to get high inhibition levels; therefore, it is improbable that enhanced dewatering will be an important effect. In lime scrubbing, reduced oxidation levels may not enhance dewatering because the

Table II. Dewatering with limestone at the EPA-RTP pilot plant.[19]

Run No.	LS-0	LS-4	LS-5
$S_2O_3^=$ (mM)	0	20.1	8.9
Cl^- (mM)	1.7	1.9	86
Ca^{++} (mM)	22	3.6	35
Oxidation (%)	20.6	1.2	1.3
Settling rate (cm/min)	0.7	2.6	3.6
Filter cake solids (%)	56	65	75
Mass median particle diameter (μm)	12	14	28
Diameter range including 90 wt% of the sample (μm)	6–21	7–24	10–50

calcium sulfite solids typically crystallize as agglomerates rather than single platelets. The tests involving Mg may have had artificially high oxidation levels because of the addition of magnesium sulfate to maintain the Mg concentration in the pilot plant. In commercial systems Mg would be added as MgO or $MgCO_3$ and would not contribute sulfate.

Mg has been reported to degrade dewatering properties of calcium sulfite solids from limestone dual alkali systems at Mg/Ca ratios as low as 30 mole/mole in the solution.[32] The RTP limestone runs promoted by Mg and by adipic acid had Mg/Ca ratios as large as 12–15 at high thiosulfate concentration where dewatering was not enhanced.

At Seminole Electric, the filter cake improved from 50 to 80 percent solids with the addition of thiosulfate to give an inhibitor product exceeding 20×10^{-6} M^3/h in the high chloride limestone scrubber.[20]

SO_2 Removal and Limestone Utilization

In systems where charge balance dictates a ratio of dissolved sulfate to calcium greater than 1 (with $2[Mg^{++}] + [Na^+] > [Cl^-]$), a reduction in gypsum saturation (caused by thiosulfate additon or otherwise) will result in a significant decrease of dissolved calcium. As a result SO_2 removal and/or limestone dissolution will occur more readily. In the tests at Shawnee,[11] dissolved calcium decreased from 22 to 3 mM with the addition of 6 mM thiosulfate. In tests without added chloride at RTP, the dissolved calcium decreased from 25 to 6 mM with limestone, from 18 to 3.5 mM with Mg-promoted limestone, and from 16 to 1 mM with Mg-promoted lime.

Reduced calcium enhances SO_2 removal by increasing dissolved sulfite alkalinity through the equilibrium reaction:

$$CaSO_3(s) \leftrightarrow Ca^{++} + SO_3^= \quad (16)$$

$$[SO_3^=] = K_{sp}/[Ca^{++}] \quad (17)$$

Dissolved sulfite reduces the liquid film resistance to mass transfer in the scrubber. This effect should be especially pronounced in Mg-promoted systems where dissolved sulfite is already high. However, the maximum enhancement of SO_2 removal is limited by gas film resistance. No effect of thiosulfate on SO_2 removal was observed at Shawnee or at RTP without Mg promotion. However at RTP with limestone promoted by 50 mM Mg, the SO_2 removal increased from 83 to 88 percent with the addition of 8 mM thiosulfate. In lime scrubbing promoted by 84 mM Mg, the SO_2 removal increased from 95 to 98 percent with the addition of 27 mM thiosulfate. At the Phillips Station of Duquesne Light, the presence of about 3 mM thiosulfate in a lime scrubber promoted by MgO enhanced SO_2 removal from 83 to 88 percent.[7]

Reduced dissolved calcium should also enhance limestone dissolution and increase equilibrium pH in the hold tank through the reaction:

$$CaCO_3(s) + 2H^+ \rightarrow Ca^{++} + CO_2 + H_2O \quad (18)$$

$$[H^+]^2 = K[Ca^{++}]P_{CO_2} \quad (19)$$

In the Shawnee tests,[11] the hold tank pH was controlled at 5.8 as thiosulfate concentration was increased to 6 mM and the limestone utilization increased from 75 to 90 percent. In the RTP work the pH was controlled at 5.5 as thiosulfate was added. With limestone alone or with 14 mM adipic acid, the limestone utilization increased from 86 to 97 percent with the addition of 20 mM thiosulfate. With 51 mM Mg, the limestone utilization increased from 88 to 94 percent with the addition of 62 mM thiosulfate. Because Mg^{++} inhibits limestone dissolution,[32,33] the effect of thiosulfate on limestone utilization will not be as great in Mg-promoted systems. If limestone utilization is held constant as thiosulfate is added to the system, the hold tank pH should increase and SO_2 removal should be enhanced by increased dissolved bicarbonate.

The use of thiosulfate tends to increase the accumulated concentration of Mg by increasing dissolution of $MgCO_3$ in the limestone and by enhancing dewatering of waste solids. At Shawnee the Mg concentration increased from 28 to 40 mM with an inhibitor product of 2×10^{-6} M^3/h.[11] At RTP the Mg concentration increased from 13 to 40 mM with an inhibitor product of 10^{-6} M^3/h.[19]

Organic Acid Makeup Rate

The makeup rate for organic acid additive, such as adipic acid or dibasic waste acid (DBA), may be reduced by the addition of thiosulfate. Improved dewatering of waste solids should reduce solution losses of additive. Oxidative degradation of organic acids is proportional to sulfite oxidation and should be reduced to the extent that thiosulfate inhibits oxidation.[8] Loss of organic acid by coprecipitation with calcium sulfite is inversely proportional to dissolved calcium.[30] However, coprecipitation losses increase as solids oxidation decreases.[31]

A series of runs was performed at RTP with a constant rate of adipic acid addition (4.2 mmole/mole SO_2 absorbed) to a limestone scrubber. The steady state adipic acid concen-

Table III. Estimated thiosulfate makeup for typical applications. Basis: 50% solids without thiosulfate, 50 mM/h SO_2 loading in hold tank.

Case	Solution composition (mM) Ca^{++}	$S_2O_3^=$	$S_3O_6^=$	Gypsum Sat. (%)	Filter cake (% solids)	Makeup (mmole/mole SO_2)
$CaCO_3$	6	3.5	12	10	55	1.6
	2	30	10	1	80	1.3
+ Chloride	100	0.6	10	1	80	0.3
+ MgO	4	15	12	10	55	1.7
	1	60	10	1	80	2.0
CaO (pH 7.5)	5	20	20	10	50	5.2
+ Chloride	100	1	20	10	50	2.7
+ MgO (pH 6.5)	5	12	15	10	50	3.5

tration was about 14 mM for a range of thiosulfate from 0 to 20 mM with very little change in the filter cake solids concentration. Losses of adipic acid by degradation and coprecipitation were about 1.8 mmole/mole SO_2 absorbed. This result suggests that the expected reduction in degradation was balanced by an increase in coprecipitation. Assuming that none of the unexplained losses are due to degradation when using greater than 5 mM thiosulfate, the extent of coprecipitation corresponds to 1.0 ppm adipic acid in solids per ppm adipic acid solution. This value is close to that predicted from previous data on coprecipitation.[30,31] Higher levels of thiosulfate in combination with adipic acid should reduce adipic acid makeup by reducing solution content in the waste solids.

Thiosulfate Degradation and Makeup

Makeup of thiosulfate is necessary to replace losses of thiosulfate and trithionate in solution entrained with waste solids. As thiosulfate inhibits oxidation, it is oxidized to tetrathionate. Tetrathionate reacts quickly with sulfite to make trithionate and regenerate some thiosulfate. Trithionate hydrolyzes slowly to make sulfate and regenerate the rest of the thiosulfate. The trithionate accumulates to a steady state concentration of 5 to 20 mM. Actual makeup costs vary from $0.20 to $3.00/tonne limestone and $3.00 to $14.00/tonne lime.

Thiosulfate Oxidation

Most oxidizing environments, including iodine (I_2), cupric (Cu^{++}), hydrogen peroxide (H_2O_2), and electrochemical anodes, convert thiosulfate initially to tetrathionate ($S_4O_6^=$).[23] Thiosulfate oxidation probably occurs by reaction of thiosulfate with a free radical to form a thiosulfate radical (Reaction 3), followed by second order reaction of thiosulfate radicals to give tetrathionate (Reaction 4). The measured rate of Reaction 4 (3.5×10^9 M^{-1} sec^{-1}, 8×10^8 M^{-1} sec^{-1})[34,35] is comparable to the rates of other radical terminating reactions involving sulfite radical (SO_3^-) or peroxymonosulfate radical (SO_5^-).[36]

In the presence of sulfite, tetrathionate is rapidly converted to trithionate by the reversible reaction:

$$S_4O_6^= + SO_3^= \rightleftharpoons S_3O_6^= + S_2O_3^= \quad (20)$$

The forward rate of this reaction has been measured by Owens[18] at 50°C and pH 4.5–5.5 in 0.3 M Na_2SO_4 with 0.01 M S(IV) and 0.0125 M $Na_2S_4O_6$. The activation energy was estimated to be 13.4 kcal/gmol using Davis[37] (Equation 4c). The effect of ionic strength attributed to cations (I_2) was taken from Rochelle[34] (Figures 3 and 4). Owens' data are correlated by:

$$r_f = k_f[S_4O_6^=][SO_3^=](M/s) \quad (21)$$

$$k_f = 7.3 \times 10^9 \exp[51_+^{0.5}/(1 + I_+^{0.5}) - 6755/T] \quad (22)$$

Earlier measurements at lower ionic strength (8–16 mM), 0°C, and pH 9 gave a proportionality constant of 9×10^9 M^{-1} s^{-1} compared to 7.3×10^9.[39] Measurements at pH 1.7, 10–40°C, and $I_+ = 2$ M, gave much lower rates and suggest that bisulfite does not react with tetrathionate as fast as sulfite.[40] Similarly the reverse rate of Reaction 20 is given by[41–43]:

$$r_r = k_r[S_3O_6^=][S_2O_3^=](M/s)$$

$$k_r = 2.2 \times 10^4 \exp[51_+^{0.5}/(1 + I_+^{0.5}) - 6417/T] \quad (23)$$

The equilibrium for Reaction 20 can be determined by setting the reverse rate equal to the forward rate:

$$K = ([S_3O_6^=][S_2O_3^=])/([S_4O_6^=][SO_3^=])$$

$$= 3.3 \times 10^5 \exp(-327/T) \quad (24)$$

At 50°C the equilibrium constant is 1.2×10^5. With 1 mM sulfite, 10 mM thiosulfate, and 10 mM trithionate, the equilibrium tetrathionate concentration is only 10^{-5} mM and the pseudo-first-order forward rate constant is 0.4 min^{-1}. Therefore, at most conditions tetrathionate is converted very quickly to trithionate. At very low sulfite (at low pH or at points where all of the sulfite is lost to oxidation), it may be possible to get a significant concentration of tetrathionate.

Owens[18] measured the net rate of oxidation of thiosulfate to trithionate at 50°C in 0.3 M Na_2SO_4 with 3 to 30 mM S(IV):

$$S_2O_3^= + SO_3^= + 0.5O_2 + H_2O \rightarrow S_3O_6^= + 2OH^- \quad (25)$$

Assuming that thiosulfate terminates all of the free radicals formed in sulfite oxidation, the rate of Reaction 20, r_{deg}, is equal to half the rate of free radical initiation, r_i. At higher thiosulfate concentrations ($[S_2O_3^=]/[S(IV)] > 0.1$), Owens found that the thiosulfate degradation rate, r_{deg}, was independent of thiosulfate concentration. His results were not always reproducible, but suggest degradation rates from 0.4 to 1 mM/h at pH 5 with greater than 0.001 mM Fe. The degradation rates appeared to be somewhat higher at pH 6 (0.4 to 2 mM/h) and somewhat lower at pH 4.5 (0.2 to 0.7 mM/h).

At lower concentrations of thiosulfate ($[S_2O_3^=]/[S(IV)] < 0.1$), Owens found that the thiosulfate degradation rate increased as thiosulfate concentration decreased. At pH 5 the rate of degradation was correlated with the rate of sulfite oxidation by:

$$r_{deg}(M/h) = 6.2([Fe]r_{ox})^{0.5}\,(M/h) \quad (26)$$

Hydrolysis of Trithionate

At pH 2 to 12 trithionate reacts slowly with water to regenerate thiosulfate[43–51]:

$$S_3O_6^= + H_2O \rightarrow S_2O_3^= + SO_4^= + 2H^+ \quad (27)$$

$$r_h = k_h[S_3O_6^=] \quad (28)$$

A number of investigators[43–51] have measured the first order constant for this reaction as a function of temperature. The best data are probably those of Naito *et al.*[43] which give a rate of 0.035 h^{-1} at 55°C. Naito's data are correlated by the equation:

$$k_h = 1.5 \times 10^{12} \exp(-10{,}166/T)(h^{-1}) \quad (29)$$

The net effect of thiosulfate oxidation (Reaction 25) and hydrolysis (Reaction 27) is oxidation of S(IV) to sulfate, with no loss of thiosulfate. In a scrubber system where thiosulfate oxidation and hydrolysis both occur in the same well-mixed solution volume, for example the hold tank, the trithionate concentration should reach a steady state concentration given by:

$$[S_3O_6^=] = r_{deg}t/(1 + k_ht) \quad (30)$$

The system residence time, t, is defined as the ratio of system solution volume (hold tank + thickener) to the rate of solution loss from the system (filter cake + other losses). With large residence time (>100 h), typical systems with good dewatering, the steady state trithionate concentration is independent of residence time and is given by:

$$[S_3O_6^=] = r_{deg}/k_h \quad (31)$$

At 55°C with $r_{deg} = 0.5$ mM/h, the trithionate concentration should be 14 mM. To the extent that oxygen is unavailable at locations such as the thickener, hydrolysis will occur but thiosulfate oxidation will not. Therefore steady state trithionate concentration will be proportionately smaller.

Battelle has analyzed solutions from three of the Shawnee runs with thiosulfate by modified ion chromatographic

methods for dithionate and polythionates.[14] These analyses were made several months after the samples were collected and may not be representative. They found 3 to 4 mM trithionate and 0.5 to 1 mM dithionate in most of the samples. Only one sample of thickener overflow had a significant concentration of other polythionates (1.3 mM tetrathionate).

With data from Shawnee and RTP, the steady state concentration of trithionate and other degradation products can be estimated by difference from total sulfur analyses and by difference from sodium analyses assuming a constant background level of sodium. At Shawnee the concentration of degradation products (expressed as trithionate) was 6–10 mM from total sulfur and about 10 mM based on sodium analysis. Thickener underflow consistently contained 1.5–3 mM more thiosulfate and less trithionate than scrubber solution, suggesting that hydrolysis was occurring in the thickener, without corresponding thiosulfate oxidation. The earliest run at Shawnee suggested trithionate of 15 mM from total sulfur and 21 mM from sodium.[10]

At RTP total sulfur analyses were not consistent and suggest trithionate concentrations from 0 to 20 mM. Sodium balances suggest 5 to 10 mM trithionate with as much as 18 mM in the runs with lime alone. The trithionate level was not a function of thiosulfate concentration at either Shawnee or RTP. Based on the overall sodium balance the system solution residence time, t, was in the range of 110–660 hours. Therefore, Equation 26 can be used to estimate r_{deg}. Assuming that degradation occurs only in the hold tank and that hydrolysis occurs throughout the system, r_{deg} is estimated to be 0.6 mM/h for 10 mM trithionate. A comparable estimate for the recent Shawnee data gives $r_{deg} = 1.6$ mM because of the relatively larger thickener.

Makeup Requirements

Thiosulfate must be added to the system at a rate equal to solution losses of thiosulfate and equivalent trithionate. Because trithionate is usually present at a constant level, makeup rates are a weaker function of thiosulfate than might be expected. Heavy initial doses of thiosulfate have also been required at both RTP and Shawnee to provide the minimum inventory of trithionate before a significant concentration of thiosulfate could be maintained. Because thiosulfate actually degrades somewhat faster at lower concentrations and because a small change of thiosulfate makeup rate can make a large change in thiosulfate concentration, neither Shawnee nor RTP was able to maintain constant thiosulfate concentration at less than about 3 mM.

In the RTP tests, the minimum makeup rate needed to maintain some thiosulfate concentration was 1.3 mmole thiosulfate/mole SO_2 absorbed and makeup rates as high as 10.7 mmole/mole SO_2 were used to obtain 27 mM thiosulfate. However, solution losses are abnormally high at RTP. Estimates of solution losses for these two cases based on filter cake solids concentration give makeup rates of 0.7 and 2.0 mmole/mole SO_2, respectively. Makeup rates at Shawnee varied from 0.4 to 1.2 mmoles/mole SO_2. Makeup rates in the Duquesne Light scrubbers using lime promoted by MgO have been about 3.5 mmole/mole SO_2.[7] In the high chloride limestone scrubbers at Seminole Electric, thiosulfate makeup appears to be about 1.5 mmole/mole SO_2 based on preliminary results.[20]

Table III gives thiosulfate makeup rates estimated for several potential applications. At \$120/kg-mole thiosulfate, the makeup rate is about equal to the cost in dollars for thiosulfate makeup per tonne $CaCO_3$. Two different levels of thiosulfate have been included, one to get 10 percent gypsum saturation and one to get significant enhancement of solids dewatering. Thiosulfate is most attractive in limestone systems with some chlorides, where little additional thiosulfate concentration is required to enhance dewatering and thereby greatly reduce net makeup. Without chloride, enhanced dewatering can require very large increases in thiosulfate concentration which negate any reduction in solution loss.

Sources of Thiosulfate

Sodium thiosulfate is available as 30 wt percent solution at \$73/kg-mole or as anhydrous or pentrahydrate solid at \$157/kg-mole. The current production capacity is on the order of 30,000 tonne/yr with actual production closer to 15,000 tonne/yr.[52] Duquesne Light has used bags of anhydrous thiosulfate. Seminole Electric is using the solution.

Ammonium thiosulfate is an alternative direct source of thiosulfate that is produced in greater quantity (100,000 tonne/yr) at lower cost (\$70/kg-mole).[52] It is distributed as 60 percent solution. It would probably not be suitable for use in lime systems because ammonia volatility could be a problem at the high pH. Ammonia might also be an objectionable nutrient in any waste water.

Thiosulfate can also be produced in situ by reaction of sodium sulfide (Na_2S) or sodium polysulfide (Na_2S_n) with sulfite.[52,53] Sodium sulfide is available as 45 wt percent solution at an equivalent cost of \$21/kg-mole thiosulfate, assuming that 2 moles of thiosulfate can be obtained from 1 mole of sulfide. Sodium polysulfide can be prepared by dissolving elemental sulfur (powdered) in concentrated sodium hydroxide[52] or sodium sulfide solution.[54] Sodium tetrasulfide (Na_2S_4) is available as 34 wt percent solution at an equivalent cost of \$17/kg-mole thiosulfate, assuming that 3 moles of thiosulfate are obtained from 1 mole of sodium tetrasulfide.[55]

The Stretford process for removal of hydrogen sulfide from fuel gases produces a waste solution typically containing 10–25 wt percent sodium thiosulfate with 4 percent sodium sulfate, 5 percent sodium carbonate, 0.4 percent vanadium, and 0.2 percent anthraquinone disulfonate. From 1 to 5 mole percent of the sulfur absorbed by the Stretford process is converted to thiosulfate. There are 13 Stretford plants in the U.S. with the capacities greater than 15 tonne/day, amounting to a total potential thiosulfate source of 2,000–10,000 tonne of sodium thiosulfate per year.[56] This could be an inexpensive source of thiosulfate if the impurities can be tolerated.

Conclusions

1. Sodium thiosulfate is an effective additive for inhibiting sulfite oxidation. The inhibiting effectiveness is proportional to the ratio of thiosulfate and sulfite and in slurry scrubbing processes is approximately proportional to the product of thiosulfate, dissolved calcium, and SO_2 loading in the hold tank (defined as the inhibitor product). Therefore, thiosulfate is most effective in limestone scrubbers with high chloride and least effective in MgO-promoted lime scrubbers.

2. Gypsum saturation was significantly reduced and scaling was eliminated in all slurry scrubbing processes tested with an inhibitor product as low as 0.3×10^{-6} M^3/h.

3. Solids dewatering is enhanced at high levels of thiosulfate in limestone scrubbers with and without organic acids. In Shawnee tests filter cake solid increased from 65 to 85 percent and settling rates increased 0.35 to 0.65 cm/min with

an inhibitor product of 10^{-6} M^3/h. At RTP filter cake solids increased from 55 to 75 percent and settling rates increased from 0.6 to 3 cm/min at an inhibitor product of 4×10^{-6} M^3/h.

4. SO_2 removal and limestone utilization are increased by addition of thiosulfate to scrubbers with low or moderate levels of dissolved calcium. Increased SO_2 removal has been demonstrated in lime and limestone scrubbers promoted by MgO. Increased limestone utilization has been demonstrated in limestone scrubbers with low chloride.

5. The net consumption of adipic acid in a limestone scrubber was not reduced by addition of thiosulfate. Reduced degradation of adipic acid was probably offset by increased coprecipitation with calcium sulfite.

6. As thiosulfate inhibits oxidation by scavenging free radicals, it is converted to trithionate. Trithionate hydrolyzes to regenerate thiosulfate, but must accumulate to a steady state level before thiosulfate will accumulate. Therefore, the minimum addition rate of thiosulfate must provide an effective thiosulfate concentration of 10 to 20 mM. Furthermore, the scrubber must be spiked to this level before any thiosulfate concentration can be maintained.

7. Practical thiosulfate makeup rates vary from 0.3 mmole/mole SO_2 removed for limestone scrubbing with chloride to 5.2 for lime scrubbing at pH 7.5. Using sodium thiosulfate, these rates correspond to a cost range of $0.20 to $3.00/tonne limestone and $3 to $14/tonne lime.

8. Sodium thiosulfate is a practical, demonstrated additive available as concentrated solution at $73/kg-mole or as solid at $157/kg-mole. Ammonium thiosulfate, sodium polysulfide, and waste solution from Stretford processes could be used at costs as low as $17/kg-mole thiosulfate, but have not been tested.

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